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(54) LAMINATED FILM

(57)Abstract:

PURPOSE: To obtain high gas-barriering capacity by a method wherein a lamina composed of an inorganic lamellar compound in specific particle size and aspect ratio and a resinous composition including resin is put in lamination over a lamina mainly composed of ethylene-vinylalcohol copolymer.

CONSTITUTION: In a film made up by layering a lamina 1, composed of an inorganic lamellar compound and a resin over an ethylene-vinylalcohol copolymer layer 2 that is excellent in gas-barriering capacity affecting preservation of food, gas-barriering capacity is improved by increasing aspect ratio for the inorganic lamellar compound. Namely, the lamina 1, composed of the inorganic lamellar compound in particle size of 5 μ m or below and aspect ratio of 50 or above and not exceeding 5000 and a resinous composition including resin, is put in lamination over the layer 2. The inorganic lamellar compound is a lamellar compound in which a lamellar structure is formed with unit crystal laminae layered one another and is made of swelling clay mineral. The voluminal ratio of the inorganic lamellar



compound to the resin is set within a range from 5/95 to 90/10.

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CLAIMS

[Claim(s)]

[Claim 1]A laminated film in which particle diameter carries out single layer laminating of the layer which consists of a resin composition, wherein 5 micrometers or less and an aspect ratio contain 50 or more inorganic laminar compounds [5000 or less] and resin to a layer which uses an ethylene-vinylalcohol copolymer as the main ingredients at least.

[Claim 2]The laminated film according to claim 1 in which an inorganic laminar compound carries out swelling and carrying out a cleavage to a solvent with the feature.

[Claim 3]The laminated film according to claim 2, wherein an inorganic laminar compound is argillite with swelling nature.

[Claim 4]The laminated film according to claim 1, 2, or 3, wherein aspect ratios of an inorganic laminar compound are 200-3000.

[Claim 5]A laminated film given in any 1 paragraph of claims 1-4, wherein a volume ratio of (an inorganic laminar compound/resin) is the range of - (5/95) (90/10).

[Claim 6]A laminated film given in any 1 paragraph of claims 1-5, wherein resin is flood matter unity resin.

[Claim 7]The laminated film according to claim 6 in which flood matter unity resin is characterized by weight percent of a hydrogen bond nature group per resin unit weight or an ionic group being not less than 30% of 50% or less.

[Claim 8]The laminated film according to claim 6, wherein flood matter unity resin is polyvinyl alcohol or polysaccharide.

[Claim 9]The laminated film according to claim 6 by which a hydrogen bond nature group frame-common-equipment pons agent being included in a layer containing an inorganic laminar compound.

[Claim 10]The laminated film according to claim 9 in which a hydrogen bond nature group frame-common-equipment pons agent is characterized by ***** which is a zirconia compound.

[Claim 11]A layered product which has at least one layer of laminated films of a statement in any 1 paragraph of claims 1-10.

[Claim 12]A laminated film or a layered product characterized by comprising the following which consists of laminated films.

It is at least one layer about a layer which consists of resin chosen from biaxial extension polypropylene, biaxial extension nylon, and biaxial extension polyethylene terephthalate.

It is at least one layer about a laminated film given in any 1 paragraph of claims 1-10.

[Claim 13]A laminated film or a layered product given in any 1 paragraph of claims 1-12, wherein oxygen transmittance under 30 ** and 60%RH is below 0.2 cc/m^2 , day, and atm.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the laminated film excellent in GASUBARIA nature.

[0002]

[Description of the Prior Art]Although the functions for which a package is asked are various, it is the important character which influences the preservability of various gas-barrier ***** as contents protection nature, and the necessity is increasingly larger by diversification of a circulation gestalt and package art, additive regulation, change of taste, etc. And it was also a weak point of gas-barrier ** common plastic material. As a deterioration factor of foodstuffs, oxygen, light, heat, moisture, etc. are raised and oxygen is especially important as the quality of causal agents. Barrier materials are a material indispensable also for a means to control deterioration of foodstuffs, such as gas charging and a vacuum package, at the same time it intercepts oxygen effectively, By having barrier functions, such as not only oxygen gas but various kinds of gas, an organic solvent steam, fragrance, etc., it can use for rust prevention, deodorization, and the prevention from sublimation, and is used in many fields, such as foodstuffs, such as a confectionery bag, a bonito pack, a retort pouch, and a carbon dioxide beverage container, cosmetics, agricultural chemicals, and medical science.

[0003]In the film which consists of thermoplastics, films by which especially orientation was carried out, such as polypropylene, polyester, and polyamide, have the outstanding mechanical property, heat resistance, transparency, etc., and are widely used as wrapping. However, in using these films as an object for food packing. Since the interception nature of oxygen or other gases is insufficient, various problems tend to be produced with it being contents being soaked in the moisture of the external world and taste worsening [are easy to cause deterioration of the contents by oxidation degradation or aerobic bacteria or an aroma component penetrates, flavor is lost, or]. Then, the method of usually laminating the good membrane layer of other GASUBARIA nature is taken in many cases.

[0004]Various transparent plastic materials with larger GASUBARIA nature than before are also known, For example, although there are a film etc. which consist of polyvinyl alcohol, a polyethylene vinyl alcohol copolymer, and polyvinylidene chloride system resin, These plastic materials penetrate oxygen of the grade which cannot yet be disregarded to the oxygen transmittance of the metal used for canning and bottling or a glass material being almost zero.

[0005]In addition, as the method of a gas-barrier-property manifestation, there is a dispersion method of

the inorganic substance of the flat gestalt to the inside of resin, for example, to JP,62-148532,A. Polyurethane resin solution 100 of 30% of concentration using 1,6-hexane poly KABONATO diol To a weight section, mica impalpable powder 25 weight section, Coating and the manufacturing method which dries and subsequently exfoliates from a substrate are indicated on the mold-release characteristic substrate in the coating liquid composition which consists of dimethylformamide 60 weight section. To JP,64-043554,A. With the average length of 7 micrometers, the mica of the aspect ratio 140 is added, and this is poured in into chilled water, and it makes precipitate and dries [filter and] to the methanol aqueous solution of ethylene/vinyl alcohol copolymer, and is considered as a pellet, and the method of subsequently obtaining a film is indicated. further -- JP,3-93542,A -- silyl group content conversion polyvinyl alcohol -- synthetic hectorite the coating composition which is 50:50 in a weight ratio, It applies on biaxial-stretching polyethylene terephthalate (OPET), and it is made to dry and the method of heat-treating (130-150 **) is indicated. However, about GASUBARIA nature, the film obtained in these art is not yet enough, and is hard to be called what can not necessarily be satisfied.

[0006]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the mold goods of the GASUBARIA nature which has high-level gas barrier properties, and a film.

[0007]

[Means for Solving the Problem]In a film which laminated a layer which turns into an ethylene-vinylalcohol copolymer layer from an inorganic laminar compound and resin as a result of inquiring wholeheartedly, in order to solve an aforementioned problem, By enlarging an aspect ratio of an inorganic laminar compound, it found out that remarkably outstanding gas barrier property was revealed, and resulted in this invention.

[0008]That is, this invention relates to a layer which uses an ethylene-vinylalcohol copolymer as the main ingredients at a laminated film in which particle diameter carries out single layer laminating of the layer which consists of a resin composition, wherein 5 micrometers or less and an aspect ratio contain 50 or more inorganic laminar compounds [5000 or less] and resin at least. .

[0009]The inorganic laminar compound used for this invention refers to an inorganic compound in which a unit crystal layer is mutually piled up and has the layer structure. If it puts in another way, a "laminar compound" will be a compound thru/or a substance which has the layer structure, and the "layer structure" will mean structure in which a field which an atom combined strongly and arranged densely by a covalent bond etc. was piled up in parallel with weak coupling power, such as Van der Waals force. Or less [50 or more] by 5000, an aspect ratio measured by a method of mentioning an "inorganic laminar compound" usable to this invention later will not be limited, especially if particle diameter is 5 micrometers or less.

From a point of GASUBARIA nature, it is preferred that they are 100 or more (200 or more [Especially]) aspect ratios. Being revealed of the above-mentioned aspect ratio of GASUBARIA nature becomes insufficient by less than 50. It is technically difficult to obtain an inorganic laminar compound in which an aspect ratio exceeds 5000 on the other hand, and it becomes cost thru/or what is economically expensive. As for this aspect ratio, from a point of manufacture ease, it is preferred that it is 2000 (further 1500 or less) or less. As for this aspect ratio, from a point of balance of gas-barrier ***** manufacture ease, it is still more preferred that it is the range of 200-3000. It is preferred that "particle diameter" measured by a method of mentioning later from a point of film production nature at the time of considering it as a film thru/or a moldability is 5 micrometers or less. If this particle diameter exceeds 5 micrometers, a tendency

for film production nature thru/or a moldability as a resin composition to fall will arise. As for this particle diameter, from a point of the transparency of a resin composition, it is preferred that it is 3 micrometers or less. As for this particle diameter, when using a film of this invention for a use (for example, food-grade way) than to which greater importance is attached to transparency, it is especially preferred that it is 1 micrometer or less. This transparency is total light transmittance with a wavelength of 500 nm, and it is preferred that it is not less than (not less than 85 more%) 80% of grade. For example, such transparency can be suitably measured with a commercial spectrophotometer (Hitachi make and recording spectrophotometer 330 type). As an example of an inorganic laminar compound, they are graphite, a phosphate system derivation form compound (phosphoric acid zirconium system compound), and a chalcogen ghost. [It is dichalcogenate of group IV (Ti, Zr, Hf), V fellows (V, Nb, Ta), and a VI group (Mo, W), and is expressed with formula MX_2 . Here, X shows chalcogen (S, Se, Te).] A clay system mineral etc. can be raised.

[0010] Since true particle diameter measurement in a resin composition is very difficult, particle diameter of an inorganic laminar compound used by this invention is the value calculated by dynamic light scattering among a solvent. When making it fully swell with a solvent used by dynamic light scattering, and a solvent of the same kind and making it compound with resin, it is possible that particle diameter of an inorganic laminar compound in inside of resin is close to particle diameter in a solvent.

[0011] An aspect ratio (Z) of an inorganic laminar compound used by this invention is shown by relation as for which $Z=L/a$ becomes. [L is the particle diameter for which it asked by dynamic light scattering among a solvent, and a is the unit thickness of an inorganic laminar compound (unit thickness a is a value determined by powder X-ray diffractometry etc. by inorganic laminar compound independent measurement.).]. However, in $Z=L/a$, the spacing d acquired from a powder X diffraction of a constituent exists, and a relation as for which $a<d$ becomes is filled. Here, it is required for a value of d-a to be size from width of a resin single strand in a constituent. Although Z cannot necessarily be called true aspect ratio of an inorganic laminar compound in a resin composition, it has validity considerably from the following reason.

[0012] Direct measurement is very difficult for an aspect ratio of an inorganic laminar compound in a resin composition. A relation between unit thickness a decided by powder X diffraction measurement the spacing d and inorganic laminar compound independent obtained by powder X-ray diffractometry of a constituent which becomes in $a<d$ is, and if a value of d-a is more than width of a resin single strand in a constituent, It is clear that resin will be inserted between layers of an inorganic laminar compound into a resin composition, and thickness of an inorganic laminar compound has therefore become unit thickness a. Although true particle diameter measurement in a resin composition is very difficult, Considering a case where make it fully swell with a solvent used by dynamic light scattering, and a solvent of the same kind, and it is made to compound with resin. It is possible with it in a solvent that particle diameter of an inorganic laminar compound in inside of resin is quite near (however, the particle diameter L called for by dynamic light scattering.). Since it is thought that the major axis L_{max} of an inorganic laminar compound is not exceeded, it is not theoretically possible that true aspect ratio L_{max}/a is less than the definition Z of an aspect ratio in this invention. . From two points, a definition of an aspect ratio of this invention is considered [above-mentioned] to be a comparatively high thing of validity. An aspect ratio or particle diameter as

used in this invention means an aspect ratio and particle diameter which were defined above. Asakura Publishing Co., Ltd. can be referred to for details about how to ask for a and d in volumes for rock student Shuichi, a clayey encyclopedia, 35 pages or less and 271 pages or less, and 1985, for example (see [drawing 5](#) - 11 further). Although width of a resin single strand in a constituent can be asked by simulation computation etc. (for example, in the case of reference) and polyvinyl alcohol, it will be 4-5 Å about Kagaku-Dojin in Okamura et al., a high-polymer-chemistry introduction, 103 to 110 pages, and 1981 (a water molecule 2-3 Å). Thus, as for integrated intensity of a diffraction peak (it corresponds to the spacing d) observed in a powder X diffraction of a resin composition, it is preferred that it is two (further 10 or more) or more in a relative ratio to integrated intensity of a diffraction peak (it corresponds to the spacing a) used as a standard. [Drawing 5](#) is a graph which shows typically relation between an X diffraction peak of an inorganic laminar compound, and unit thickness a of this compound. [Drawing 6](#) is a graph which indicates a relation with the spacing d of this constituent typically to be an X diffraction peak of a resin composition containing an inorganic laminar compound. [Drawing 7](#) is a graph which indicates a relation with the spacing d of this constituent typically to be an X diffraction peak of a resin composition when it is difficult for a peak corresponding to the spacing d to lap with halo (or background), and to detect. In this figure, area of a portion except a baseline by the side of a low angle is made into a peak corresponding to the spacing d from 2 θ (theta is an angle of diffraction equivalent to "width of a unit thickness a + resin single strand"). [Drawing 8](#) is a graph which shows a graph and an X diffraction peak of KUNIPIA F (montmorillonite) which show an X diffraction peak of polyvinyl alcohol PVA117H / KUNIPIA F constituent. [Drawing 9](#) is a graph which shows an X diffraction peak (pattern of [drawing 6](#)) of a constituent of d= 19.62 Å of spacings. [Drawing 10](#) is a graph which shows an X diffraction peak (pattern of [drawing 6](#) and [drawing 7](#)) of a constituent of d= 32.94 Å of spacings. [Drawing 11](#) is a graph with which the spacing d shows an X diffraction peak (pattern of [drawing 7](#)) of a constituent of 44.13 Å or more.

[0013] As an inorganic laminar compound which has a big aspect ratio, swelling and an inorganic laminar compound which carries out a cleavage are preferably used for a solvent. The following "swelling and cleavage" examinations can estimate a grade of "swelling and cleavage" nature to a solvent of an inorganic laminar compound used for this invention. As for the swelling nature of this inorganic laminar compound, in the following swelling examination, it is preferred that it is a grade of about five or more (further about 20 or more). On the other hand, as for the cleavage of this inorganic laminar compound, in the following cleavage examination, it is preferred that it is a grade of about five or more (further about 20 or more). As a solvent, a solvent which has density smaller than density of an inorganic laminar compound is used in these cases. When an inorganic laminar compound is a natural expansive clay mineral, as this solvent, it is preferred to use water.

<Swelling examination>: Add the inorganic laminar compound 2g to solvent 100mL slowly (let a 100mL measuring cylinder be a container). The former (inorganic laminar compound dispersion layer) volume is read from a graduation of an interface of an inorganic laminar compound dispersion layer shaking, settlement, and 24 hours after 23 **, and a supernatant fluid. Swelling nature is so high that this figure is large.

<Cleavage examination> : The inorganic laminar compound 30g is slowly added to solvent 1500mL, Dispersion machine (the ASADA IRON WORKS CO., LTD. make, Despa MH-L, a diameter of a shuttlecock of 52 mm, and number of rotations of 3100 rpm) After peripheral speed of 8.5 m/sec distributes

for 90 minutes in distance of 28 mm between the container capacity 3L and a bottom-shuttlecock (23 **), dispersion-liquid 100mL is taken, it puts into a 100mL measuring cylinder, and volume of an inorganic laminar compound dispersion layer is read from a graduation of an interface with a supernatant fluid after 60-minute settlement. Cleavage is so high that this figure is large. As swelling and an inorganic laminar compound which carries out a cleavage, it is preferably usable to a solvent in argillite which has swelling and cleavage in a solvent. A type with which a clay system mineral generally consists of two-layer structure of having the 8th page body whorl which used aluminum, magnesium, etc. as a central metal in the upper part of a tetrahedral layer of silica, A tetrahedron layer of silica is classified into a type which consists of a three-tiered structure which sandwiched an 8th page body whorl which used aluminum, magnesium, etc. as a central metal from both sides. Kaolinite fellows, antigorite fellows, etc. can be mentioned as the former, and a smectite group, a vermiculite group, car owners, etc. can be mentioned with the number of cations between layers as the latter. Specifically Kaolinite, dickite, nacrite, halloysite, Antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, tetra cyrillic mica, a sodium TENIO light, white mica, margarite, talc, a vermiculite, phlogopite, xanthophyllite, chlorite, etc. can be raised.

[0014]Although not limited, alcohols, such as water and methanol, dimethylformamide, dimethyl sulfoxide, acetone, etc. are mentioned, and especially a solvent that swells this inorganic laminar compound has more preferred alcohols, such as water and methanol, when it is a natural expansive clay mineral, for example.

[0015]Although resin in particular used in this invention is not limited, for example Polyvinyl alcohol (PVA), An ethylene-vinylalcohol copolymer (EVOH), a polyvinylidene chloride (PVDC), polyacrylonitrile (PAN), polysaccharide, polyacrylic acid, its ester species, etc. are mentioned.

[0016]Flood matter unity resin with which it is satisfied of a rate that weight percent of a hydrogen bond nature group per resin unit weight or an ionic group is 20% - 60%, as a desirable example is raised. What satisfies a rate that weight percent of a hydrogen bond nature group per resin unit weight of flood matter unity resin or an ionic group is 30% - 50%, as a still more desirable example is raised. As a hydrogen bond nature group of flood matter unity resin, a hydroxyl group, an amino group, a thiol group, a carboxyl group, a sulfonic group, a phosphate group, etc. are mentioned, and a carboxylate group, a sulfonic acid ion group, a phosphate anion group, ammonium, phosphonium group, etc. are mentioned as an ionic group. As a still more desirable thing, a hydroxyl group, an amino group, a carboxyl group, a sulfonic group, a carboxylate group, a sulfonic acid ion group, ammonium, etc. are mentioned among a hydrogen bond nature group of flood matter unity resin, or an ionic group.

[0017]As an example, polyvinyl alcohol and a vinyl alcohol molar fraction, for example An ethylene-vinylalcohol copolymer beyond 41 mol %, Hydroxymethylcellulose, hydroxyethyl cellulose, carboxymethyl cellulose, Amylose, amylopectin, pullulan, curdlan, Zhang Tan, a kitchen, Polysaccharide, such as chitosan, cellulose, pullulan, and chitosan, polyacrylic acid, Sodium polyacrylate, polybenzenesulfonic acid, poly sodium benzenesulfonate, polyethyleneimine, polyallylamine, its ammonium salt polyvinyl thiol, polyglycerin, etc. are mentioned.

[0018]Polyvinyl alcohol and polysaccharide are raised as a still more desirable thing of flood matter unity resin. Polyvinyl alcohol used for an inorganic laminar compound contained layer of this invention is polymer which has a monomeric unit of vinyl alcohol as the main ingredients. As such "polyvinyl alcohol", For example, polymer (what became vinyl alcohol and a copolymer of vinyl acetate correctly) which can obtain

an acetate ester portion of a vinyl acetate polymer by hydrolyzing thru/or carrying out an ester interchange (saponification), A trifluorovinyl acetate polymer, a formic acid vinyl polymerization object, a vinyl pivalate polymer, Polymer produced by saponifying t-butylvinyl ether polymer, a trimethylsilyl vinyl ether polymer, etc. is raised (about details of "polyvinyl alcohol"). For example, a volume on poval meeting, "the world of PVA", 1992, Polymers Publication Meeting; Polymers Publication Meeting can be referred to in Nagano et al., poval, and 1981. Not less than 70% of a grade of "saponification" in polyvinyl alcohol is desirable at mole percentage, is still more preferred, and is still more preferred. [of not less than 98% of what is called a full saponification article] [of not less than 85% of thing] As for a degree of polymerization, 5000 or less [100 or more] are preferred (3000 or less [200 or more] are still more preferred).

[0019]Polysaccharide here is a biopolymer compounded by condensation polymerization of various monosaccharides by a living organism, and a chemical modification thing based on them is also contained here. For example, cellulose, such as cellulose and hydroxymethylcellulose, hydroxyethyl cellulose, and carboxymethyl cellulose, amylose, amylopectin, pullulan, curdlan, Zhang Tan, a kitchen, chitosan, etc. are mentioned.

[0020]When resin used by this invention is flood matter unity resin, a hydrogen bond nature group frame-common-equipment pons agent can be used in order to improve the water resisting property (meaning of barrier property after a waterproof environmental test).

[0021]Although not limited especially as a hydrogen bond nature group frame-common-equipment pons agent, for example A titanium system coupling agent, The Silang system coupling agent, a melamine system coupling agent, an epoxy system coupling agent, an isocyanate system coupling agent, a copper compound, a zirconia compound, etc. are mentioned, and a zirconia compound is mentioned more preferably.

[0022]As an example of a zirconia compound, for example Zirconium oxychloride, Zirconium halides, such as a hydroxyzirconium chloride, a zirconium tetrachloride, and zirconium bromide, Zirconium salt of mineral acid, such as zirconium sulfate, basic zirconium sulfate, and a zirconium nitrate, A formic acid zirconium, an acetic acid zirconium, a propionic acid zirconium, Zirconium salt of organic acid, such as a caprylic acid zirconium and a stearic acid zirconium, Zirconium complex salt, such as zirconium carbonate ammonium, zirconium sulfate sodium, acetic acid zirconium ammonium, and zirconium sodium oxalate, citrate zirconium sodium, and citrate zirconium ammonium, etc. are raised.

[0023]An addition of a hydrogen bond nature group frame-common-equipment pons agent is a ratio (K) of the number of mols of a bridge construction generation group of a cross linking agent (CN) to the number of mols of a hydrogen bond nature group of flood matter unity resin (HN). [Namely, $K = \text{CN}/\text{HN}$] is 0.001. If it is ten or less range above, it will not be limited in particular, but it is or more 0.01 one or less range preferably.

[0024]Although composition ratio (volume ratio) in particular of an inorganic laminar compound and resin which are used in this invention is not limited, generally, it is more preferred that ranges of a volume ratio of (an inorganic laminar compound/resin) are 5 / 95 - 90/10, and ranges of a volume ratio are 5 / 95 - 50/50. In 5 / 95 - 30/70, membranous pliability becomes good and it has an advantage, like a barrier property fall depended for breaking and bending becomes small, or peel strength becomes strong in 7 / 93 - 17/83. When a volume fraction of an inorganic laminar compound is smaller than 5/95, barrier performance is not enough, and when larger than 90/10, film production nature is not good.

[0025]A combination method of a constituent which consists of an inorganic laminar compound and resin, Although not limited in particular, beforehand liquid in which resin was dissolved, and an inorganic laminar compound, for example After mixing swelling and dispersion liquid which carried out the cleavage, A method of removing a solvent, a method of adding to resin swelling and dispersion liquid which carried out the cleavage for an inorganic laminar compound, and removing a solvent, a method of adding an inorganic laminar compound to liquid in which resin was dissolved, and removing a solvent, after carrying out a cleavage, swelling and, a method of carrying out heat kneading of resin and the inorganic laminar compound, etc. are mentioned. Front 3 persons are preferably used by making an especially big aspect ratio into a method of obtaining easily.

[0026]In front 3 above-mentioned persons' method, the water resisting property (meaning of barrier property after a waterproof environmental test) of a film especially improves by carrying out heat aging of the solvent below not less than 110 °C after removal from a system. Although there is no limitation in aging time, a film needs to reach preset temperature at least, for example, in the case of a method by thermal contact like hot air drying equipment, 100 or less minutes is preferred 1 second or more. There is no limitation in particular also about a heat source, and various things, such as hot calender roll contact, thermal contact (air, oil, etc.), infrared heat, and heat by microwave, can be applied. Especially a waterproof effect here is remarkably high when it is the argillite in which an inorganic laminar compound has swelling nature when resin is flood matter unity resin.

[0027]It can obtain what carried out copolymerization of ethylene and the vinyl acetate by the ability of saponification processing of the ethylene-vinylalcohol copolymer used for this invention to be carried out. As for a molar fraction of ethylene, 20-60-mol% of the range is used preferably. Film-ization is performed by the usual extrusion molding, such as inflation molding. There is no limitation in film thickness and that by which stretching treatment is carried out is also used preferably. It can obtain what carried out copolymerization of ethylene and the vinyl acetate by the ability of saponification processing of the ethylene-vinylalcohol copolymer used for this invention to be carried out. As for a molar fraction of ethylene, 20-60-mol% of the range is used preferably. Film-ization is performed by the usual extrusion molding, such as inflation molding. There is no limitation in film thickness and that by which stretching treatment is carried out is also used preferably.

[0028]Limitation in particular is not carried out as a method of laminating a layer which contains an inorganic laminar compound in a layer which uses an ethylene-vinylalcohol copolymer as the main ingredients. A coating method which performs coating liquid of a constituent in a layer which uses an ethylene-vinylalcohol copolymer as the main ingredients, and carries out spreading, desiccation, and heat treatment to a base material surface, a method of laminating later a layer containing an inorganic laminar compound, etc. are preferred. As for both interface, processing of corona treatment, an anchor coat agent, etc. may be carried out. As a coating method, the direct photogravure method, the reverse photogravure method, and the micro photogravure method, Methods, such as a coating method which combined the roll coating methods, such as the 2 roll beat coat method and the bottom product three feeding reverse coat method, and the doctor knife method and the die coat method, a dip coating method, the BAKOTINGU method, and these, are mentioned. Although film thickness does not have limitation in particular, 10 micrometers or less are preferred at dried thickness, and 1 more micrometer or less is more preferred (since the transparency of a layered product also doubles and has the strong point in which it is remarkable

and high, in 1 micrometer or less, for a required use of transparency, it is still more desirable.). Although there is no restriction in particular about a minimum, in order to acquire the effective gas-barrier effect, it is preferred that it is 1 nm or more.

[0029]A substrate in particular of a laminated film is not limited, but common substrates, such as resin, paper, aluminum foil, wood, cloth, and a nonwoven fabric, are mentioned. As resin used as a substrate, polyethylene (low density, high density), Ethylene propylene rubber, an ethylene-butene copolymer, an ethylene-hexene copolymer, An ethylene-octene copolymer, polypropylene, an ethylene-vinylacetate copolymer, Polyolefin system resin, such as an ethylene-methyl methacrylate copolymer and ionomer resin, Polyester system resin, such as polyethylene terephthalate, polybutylene terephthalate, and polyethylenenaphthalate, Nylon 6, nylon 6, 6, meta xylenediamine adipic acid polycondensation polymer, Amide system resin, such as polymethyl methacrylic imide, polymethylmethacrylate, Which acrylic resin, polystyrene, a styrene acrylonitrile copolymer, Styrene, such as a styrene acrylonitrile butadiene copolymer and polyacrylonitrile, Hydrophobing cellulose type resin, such as acrylonitrile series resin, Tori cellulose acetate, and JI cellulose acetate, Hydrogen bond nature resin, such as halogen containing resin, such as polyvinyl chloride, a polyvinylidene chloride, polyvinylidene fluoride, and Teflon, polyvinyl alcohol, an ethylene-vinylalcohol copolymer, and a cellulosic, Engineering-plastics system resin, such as polycarbonate resin, polysulphone resin, polyether sulfone resin, polyether ether ketone resin, polyphenylene oxide resin, polymethylene oxide resin, and liquid crystal resin, etc. are raised.

[0030]In a layered product in a film gestalt, in these, as an outer layer, Polypropylene which carried out the coat of the polyvinylidene chloride called polypropylene, polyethylene terephthalate and nylon by which biaxial stretching was carried out, and K coat and by which biaxial stretching was carried out, They are preferably arranged by polyethylene terephthalate, nylon, etc. and to a inner layer. Polyolefin system resin since heat-sealing nature is generally good, For example, polyethylene (low density, high density), ethylene propylene rubber, An ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, polypropylene, an ethylene-vinyl acetate copolymer, an ethylene-methyl methacrylate copolymer, ionomer resin, etc. are used preferably.

[0031]This invention is a range which does not spoil an effect of ****, and may mix various additive agents, such as an ultraviolet ray absorbent, colorant, and an antioxidant. This invention contains a laminated film and a layered product which have at least one layer of laminated film layers described in a top.

[0032]
[Effect of the Invention]According to this invention, an ethylene-vinylalcohol copolymer in the layer used as the main ingredients. If it is resin and an inorganic laminar compound, it becomes possible to obtain the gas barrier laminated film which has unprecedented high-level gas barrier properties by laminating the becoming layer [aspect ratio] the particle diameter of the inorganic laminar compound having used 5 micrometers or less, and using or more 50 5000 or less thing. As described in the example, only the layer which uses an ethylene-vinylalcohol copolymer as the main ingredients shows the oxygen transmittance of 1 cc/m² and a day-atm level under standard environment, but. The invention in this application is oxygen transmittance lower a single figure than this, and it has unimaginable high-level barrier property from an old material. The laminated film of this invention from exceeding resin greatly and approaching the barrier property of metal or ceramics in barrier property. Metal and inorganic materials, such as aluminum foil and glass, can be used also for the use made indispensable from a viewpoint of barrier property, It can be said

to be the material which smashes the common sense of an old barrier property resin composition (about weak points, such as metalead opacity and brittleness of ceramics, it cannot be overemphasized that this invention which is a resin composition is superior to them.). Namely, the film of this invention as wrapping, As a food-grade way, bean paste, pickles, a daily dish, baby food, food boiled down in soy, konnyaku, A fishcake tube, boiled fish paste, a processed marine product, a meatball, a hamburger, Genghis Khan, A ham, a sausage, other meat processed goods, green tea, coffee, tea, a dried bonito, Oil confectionery, such as tangle flakes and a potato-chips buttered peanut, a rice confectionery, A biscuit, Cookie, a cake, steamed filled dumplings, sponge cake, a cheese head, butter, It is extensively used for end rice cake, soup, sauce, ramen noodles, etc., and is further used for the use extensive to industrial material packages of medical science, an electron, chemicals, machinery, etc., such as a semiconductor package, an oxidizing medicine package, and a precision material package, etc. else [, such as pet food, agricultural chemicals and manure, and an infusion solution pack].

[0033]

[Example] Hereafter, although an example explains this invention in detail, this invention is not limited to these. The measuring method of various physical properties is described below.

[Oxygen transmittance] It measured at an oxygen transmittance measuring device (OX-TRAN 10/50A, product made by MOCON), and the temperature of 30 °C (20 °C of gas conditioning thermostats) (relative humidity showed about 60%).

[Thickness measurement] 0.5 micrometers or more were measured with the digital thickness meter. Less than 0.5 micrometer Gravimetric analysis (the gravimetry value of the film of a definite area was measured in the area, and it was determined by constituent specific gravity further.). Or in the case of the constituent of this invention, and the layered product of a substrate etc., it was based on the ultimate analysis method (how to calculate the ratio of the resin composition layer of this invention to a substrate from the ratio of the specific inorganic matter ultimate analysis value (constituent layer origin) of a layered product to an inorganic laminar compound independent specific element molar fraction).

[Particle diameter measurement] It measured on condition of an ultrafine particle grading analysis meter (BI-90, made in Brookhaven), the temperature of 25 °C, and an aqueous solvent. The central diameter for which it asked from the photon correlation method by dynamic light scattering was made into the particle diameter L.

[Aspect ratio calculation] The diffractometry by the powder method of an inorganic laminar compound independent and a resin composition was performed using X-ray diffractometer (XD-5A, Shimadzu make). This searched for the spacing (unit thickness) a of the inorganic laminar compound, and it checked that there was a portion into which the spacing of the inorganic laminar compound has spread from the diffractometry of a resin composition further. It was with the particle diameter L for which it asked by the above-mentioned method, and the formula of $Z=L/a$ determined aspect ratio Z.

[Example 1] Synthetic mica (tetra cyrillic mica (NA-TS); product made from Topy Industries, Ltd.) is distributed so that it may become 0.65wt% at ion exchange water (below 0.7 mS/cm), and let this be inorganic laminar compound dispersion liquid (A liquid). a value with which the particle diameter of the synthetic mica (NA-TS) concerned is obtained from 977 nm and a powder X diffraction is 0.9557 nm, and aspect ratio Z is 1043. Polyvinyl alcohol (PVA117H; Kuraray make, the degree of saponification; 99.6%, degree of polymerization 1700) is dissolved in ion exchange water (below 0.7 mS/cm) so that it may

become 0.325 wt%, and let this be a resin solution (B liquid). A liquid and B liquid were mixed so that each formed element ratio (volume ratio) might be set to inorganic laminar compound/resin = 3/7, and this was made into coating liquid. a 15-micrometer-thick ethylene-vinylalcohol copolymer film (Eval EF-F; made by Kuraray) top -- presentation liquid -- photogravure coating (test coating-machine; -- : by Yasui Seiki Co. -- a micro photogravure coating method.) By 3-m/in coating speed, 80 ° (entrance-side heater) 100 ° (outlet side heater) drying temperature carried out, and the laminated film was obtained. The dried thickness of the coating layer concerned was 0.8 μm. The oxygen transmittance in 30 ° of this laminated film and 60%RH was 0.09 cc/m² / day. (1st Table)

[Examples 2-6] With the composition which showed the heat treatment condition after the ratio of a substrate, an inorganic laminar compound, resin, and an inorganic laminar compound and resin, a hydrogen bond nature group frame-common-equipment pons agent, and film production in the 1st table, respectively, by the method of Example 1, the laminated film was produced and the oxygen transmittance examination was done. The result was excellent in GASUBARIA nature as shown in the 1st table.

[Example 7] as a hydrogen bond nature group frame-common-equipment pons agent, Zirconium carbonate ammonium (first Jill Kozol AC7 made from rare element industrial (it is 15wt% by zirconium oxide conversion water content solution)) was added to the mixed liquor of A liquid B liquid so that it might become a ratio of 1 mol of zirconium elements to 15 mol of hydroxyl groups of polyvinyl alcohol. Others were the composition described in the 1st table, and also did the oxygen transmittance examination like Example 1. The result was excellent in GASUBARIA nature as shown in the 1st table.

[Example 8] as a hydrogen bond nature group frame-common-equipment pons agent, Zirconium carbonate ammonium (first Jill Kozol AC7 made from rare element industrial (it is 15wt% by zirconium oxide conversion water content solution)) was added to the mixed liquor of A liquid B liquid so that it might become a ratio of 1 mol of zirconium elements to 15 mol of hydroxyl groups of polyvinyl alcohol. Others were the composition described in the 1st table, and also heat-treated 140 ° of films after film production like Example 1 for 10 minutes. As a result of doing an oxygen transmittance examination, it excelled in GASUBARIA nature as shown in the 1st table.

[Example 9] Urethane system adhesives (made in transformation [Mitsuhiro] : YUNO flex time J3) were used for the inorganic laminar compound contained layer of the laminated film obtained in Example 1, dry laminate of the non-stretched polypropylene film (Toyobo make: pi-wren film CT60 micrometers in thickness) was carried out, and the laminated film was obtained. The oxygen transmittance in 30 ° of this laminated film and 60%RH is below 0.1 cc/m² / day.

It excelled also in heat-sealing nature and transparency.

[Comparative example 1] It is made to dissolve not using inorganic laminar compound dispersion liquid (A liquid), so that it may become 1wt% at polyvinyl alcohol (PVA117H; Kuraray make, the degree of saponification; 99.6%, degree of polymerization 1700), Except having made this into the resin solution (B liquid), the film was obtained like Example 1 and the oxygen transmittance examination was done. The result was inferior to GASUBARIA nature as shown in the 1st table.

[Comparative example 2] The oxygen transmittance examination of the 15-micrometer-thick ethylene-vinylalcohol copolymer film (Eval EF-F; made by Kuraray) was done. The result was inferior to GASUBARIA nature as shown in the 1st table.

[Comparative example 3] Other than not using a resin solution (B liquid), although the film was produced like Example 1, the powder of synthetic mica exfoliated from the laminated film, the crack was conspicuous in the film surface, and a good laminated film was not obtained.

[0034]

[Table 1]

	基材 (厚み μm)	無機物含有層 [体積比] (厚み μm)	融点通過度 (30℃, 60SRH) $\text{cc}/\text{m}^2 \cdot \text{d} \cdot \text{atm}$
実施例 1	EF-F(15)	HA/H(3/7) (0.8)	0.1以下
実施例 2	EF-F(15)	F/H(3/7) (0.8)	0.1以下
実施例 3	EF-E(15)	F/H(4/8) (0.8)	0.1以下
実施例 4	EF-E(15)	F/H(2/8) (0.8)	0.1以下
実施例 5	EF-F(15)	F/H(1.5/8) (0.8)	0.1以下
実施例 6	EF-F(15)	F/H(1/8) (1.3)	0.1以下
実施例 7	EF-F(15)	F/H(2/8) (0.8) Z	0.1以下
実施例 8	EF-F(15)	F/H(1.5/8) (0.8) 2A	0.1以下
比較例 1	EF-F(15)	H(0.8)	0.8
比較例 2	EF-F(15)	なし	1.0

Cable address

EF-F: Ethylene-vinylalcohol copolymer film (Kuraray make: name-of-article Eval EF-F, ethylene 32 mol %)

EF-E: Ethylene-vinylalcohol copolymer film (Kuraray make: name-of-article Eval EF-E, ethylene 44 mol %)

Na: Tetra cyrillic mica pulverization article (Topy Industries: name of article NaTs)

F: Natural montmorillonite (Kunimine Industries: name-of-article KUNIPIAF)

H: Polyvinyl alcohol (Kuraray make: poval 117H, degree-of-polymerization 1700, and saponification degree % of 99.6 mol)

Z: Zirconium carbonate ammonium solution (first product made from rare element industry : Jill Kozol AC7)

A: Heat-treat 140 ** of laminated films (after desiccation) for 10 minutes.

[Translation done.]

* NOTICES *

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damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]Drawing 1 is one key map of the lamination of the section of the laminated film of this invention.

[Drawing 2]Drawing 2 is one key map of the lamination of the section of the laminated film of this invention.

[Drawing 3]Drawing 3 is one key map of the lamination of the section of the laminated film of this invention.

[Drawing 4]Drawing 4 is one key map of the lamination of the section of the laminated film of this invention.

[Drawing 5]Drawing 5 is a graph which shows typically the relation between the X diffraction peak of an inorganic laminar compound, and unit thickness a of this compound.

[Drawing 6]Drawing 6 is a graph which indicates a relation with the spacing d of this constituent typically to be an X diffraction peak of the resin composition containing an inorganic laminar compound.

[Drawing 7]Drawing 7 is a graph which indicates a relation with the spacing d of this constituent typically to be an X diffraction peak of a resin composition when it is difficult for the peak corresponding to the spacing d to lap with halo (or background), and to detect.

[Drawing 8]Drawing 8 is a graph which shows the graph and the X diffraction peak of KUNIPIA F (montmorillonite) which show the X diffraction peak of a polyvinyl alcohol PVA117H/KUNIPIA F constituent.

[Drawing 9]Drawing 9 is a graph which shows the X diffraction peak (pattern of drawing 6) of the constituent of $d = 19.62$ Å of spacings.

[Drawing 10]Drawing 10 is a graph which shows the X diffraction peak (pattern of drawing 6 and drawing 7) of the constituent of $d = 32.94$ Å of spacings.

[Drawing 11]Drawing 11 is a graph with which the spacing d shows the X diffraction peak (pattern of drawing 7) of a constituent of 44.13 Å or more.

[Description of Notations]

1 The layer containing an inorganic laminar compound

Two ethylene-vinylalcohol copolymer layers

3 The substrate for lamination

[Translation done.]